SIMULATION AND VALIDATION OF ADSORPTION PROCESS FOR ACRYLIC ACID REMOVAL FROM WASTE WATER

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ABSTRACT

The objectives of this study were to develop the mathematical model of the adsorption process of the acrylic acid removal and also to validate the simulation of the adsorption process by using the previous experimental data. The adsorption process is used in the waste water treatment to remove toxic or organic pollutants. Simulation of the adsorption process is necessary to understand the acrylic acid removal using adsorption process. Acrylic acid is removed from the waste water because it can cause serious damage to the environment due to its high toxicity for the aquatic organisms. As a conclusion, the objective is achieved. The new mathematical model of the adsorption process of the acrylic acid by using the activated carbon can created based on the mass balance on the continuous fixed bed column. The validation of the simulation is carried out to compare the simulation data with the experiment data. This research is to improve the understanding of adsorption process of acrylic acid removal from waste water by created the mathematical modeling.

SIMULASI DAN PENGESAHAN PENJERAPAN PROSES UNTUK PENYINGKIRAN ASID AKRILIK DARI AIR SISA RAWATAN

ABSTRAK

Objektif kajian ini adalah untuk membangunkan model matematik proses penjerapan penyingkiran asid akrilik dan juga untuk mengesahkan simulasi proses penjerapan dengan menggunakan data sebelumnya eksperimen. Proses penjerapan digunakan dalam rawatan air sisa rawatan untuk membuang bahan pencemar toksik atau organik. Simulasi proses penjerapan adalah perlu untuk memahami penyingkiran asid akrilik menggunakan proses penjerapan. Akrilik asid dikeluarkan daripada air sisa rawatan kerana ia boleh menyebabkan kerosakan yang serius kepada alam sekitar akibat ketoksikan yang tinggi untuk organisma akuatik. Sebagai kesimpulannya, objektif dicapai. Model baru matematik proses penjerapan asid akrilik dengan menggunakan karbon diaktifkan boleh diwujudkan berdasarkan imbangan jisim pada turus tetap berterusan. Pengesahan simulasi dijalankan untuk membandingkan data simulasi dengan data eksperimen. Kajian ini adalah untuk meningkatkan pemahaman proses penjerapan penyingkiran asid akrilik dari air sisa oleh mencipta pemodelan matematik.

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a_p	Radius of the adsorbent pellets, m
b	Langmuir isotherm parameter, ml/mg
c	Solute concentration in the liquid phase inside the pores, mg/l
C_b	Bulk phase dye concentration, mg/ml
C_s	Liquid phase concentration in equilibrium with qs on the surface, mg/ml
C_{bo}	Inlet adsorbate concentration, mg/ml
D_L	Axial dispersion coefficient, m^2/s
k_f	External film mass transfer coefficient, m/s
L	Column length, m
q	Average adsorbed phase dye concentration, mg/g
q_m	Langmuir isotherm parameter, mg/g
q_p	Concentration on the surface of the pellet, mg/g
r	Radial coordinate, m
t	Time, sec
V	Superficial velocity, m/s
z	Axial coordinate, m
ε	Bed porosity

CHAPTER 1

INTRODUCTION

1.1 Background

Adsorption is typically used in wastewater treatment to remove toxic or recalcitrant organic pollutants (especially halogenated but also non-halogenated), and to a lesser extent, inorganic contaminants, from the wastewater. Adsorption finds applications in tertiary wastewater treatment as a polishing step before final discharge. Adsorption is commonly used in the treatment of industrial wastewaters containing organic compounds not easily biodegraded during secondary (biological) treatment or toxic. In the adsorption process, acrylic acid is removed from waste water by using the activation carbon. The activation carbon has ability to remove the contaminants from the water. Acrylic acid is removed from waste water because it contain high toxicity that can harmful the aquatic organism. The adsorption process is used in the waste water treatment because it has low cost operation and has high efficiency.

Acrylic acid is also known as propenoic acid which has a colorless transparent liquid which a pungent smell. The boiling point of acrylic acid is 141.0

^oC and the melting point is 13.5 ^oC. Its density is 1.045 g/ml. Acrylic acid is produced from propene which is a byproduct of ethylene and gasoline production. This corrosive chemical is miscible in water, alcohol, and esters and polymerizes readily in the presence of oxygen forming acrylic resins. Acrylic acid is a strong corrosive agent to many metals, such as unalloyed steel, copper and brass. Acrylic acid undergoes reactions characteristics of both unsaturated acids and aliphatic carbolic acids or esters. Acrylic acids also can be polymerizing very easily. The polymerization is catalysed by heat, light, and peroxides and inhibited by stabilizers, such as monomethyle ether of hydroquinone or hydroquinone. These phenolic inhibiters are effective only in the presence of oxygen. The highly exothermic, spontaneous polymerization of acrylic acid is extremely violent. Acrylic acid is widely used in several industries such as painting, chemical fibers, adhesives, paper, oil additives and also detergent. When the acrylic acid released in effluents serious damaged to the environment can be cause because it has high toxicity for aquatic organisms.

The industries nowadays gives severe impact to our nature by producing a lot of pollution that have the tendency to brings more harmful than good such as air pollution, sound pollution and water pollution. Water pollution is one of the serious environmental issues because it can cause problem to the clean water production and also can contributes to the shortage of clean water supplies. Water pollution occurs when the physicals and chemicals properties of the water are change or in the other word is, there is a contamination in the water such as lakes, rivers, oceans and also ground water.

Wastewater pollution is always consider as dangerous because it has been affected by the hazardous or dangerous chemicals and release to the water source such as rivers, lakes and oceans. The lack of clean water has always been an issue of environmental concern all over the world. This environmental issue is mainly stressed in developing countries today. Just imagine what would happen for the future life if no action will take to control the wastewater pollution. It can affect our sustainable nature and at the same time our source of clean water is not enough to meets the needs of the human from days to days. The wastewater pollution is commonly produced by domestic residences, commercial properties, industry, and agriculture. The unwanted contaminant in the wastewater can be dangerous to the aquatic and human health. It might contain the heavy metal in different concentrations and pH values that are dangerous. There are many industries that contribute to the wastewater pollution and textile industry is a part of it.

There are several ways to treat the waste water. It consists of physical, chemical and biological method. Microbial degradation, activated sludge and bio film process are the examples of biological method, which accepted for its potentialities but applicable only to lower concentration range. Meanwhile, the chemical and physical methods such as solvent extraction, precipitation, filtration, adsorption, and chemical oxidation are normally used to treat pollutants especially organic compounds and heavy metals. Every particular method is based on the application to the solute concentration range, capacity, cost, reusability and the reproducibility (Kentish & Stevens, 2001; Sarkar et al., 2003; Abburi, 2003).

1.2 Problem Statement

The acrylic acid is need to remove from waste water because it contains high amount of toxicity that can harmful the aquatic organism. Therefore, the suitable method of separation process needs to select. The adsorption process is chosen as the suitable separation process because it has high efficiency of the product and low cost of production. It is necessary to understand the adsorption process of acrylic acid using certain kind of adsorbent in order to create the mathematical modeling by using Mat Lab software. Several parameters of the adsorption process need to be investigated including adsorption time and the concentration of the adsorbate which is acrylic acid.

1.3 Research Objectives

1.3.1 To develop the mathematical modeling of the adsorption process of the acrylic acid removal.

1.3.2 To validate the simulation of the absorption process by using the experimental data.

1.4 Research Questions/Hypothesis

1.4.1 How to develop the mathematical model of the adsorption process of the acrylic acid?

1.4.2 How to validate the simulation of the absorption process by using the experimental data?

1.5 Scope of Proposed Study

This research project is focusing on the simulation and the mathematical model based on the several parameters of the adsorption process such as the adsorption time and the concentration of the adsorbate that depends on the initial controller which is the initial concentration of the adsorbate itself. The simulation is run by using the Mat Lab software that is running in the ordinary differential equation (ODE). Then, the validation of the adsorption process for acrylic acid removal from waste water is simulating by using the previous experimental data that has been done by senior UMP.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption Process

Adsorption is a process where a solid is used for removing a soluble substance from the water. In this process active carbon is the solid (Richardson et al, 2002). Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid which is called as adsorbent or the material doing adsorbing, forming a molecular or atomic film which is called as the adsorbate or material that being adsorbed (Richardson et al, 2002). It is different from absorption, in which a substance diffuses into a liquid or gases. The term sorption encompasses both adsorption and absorption processes, while desorption is the reverse process. Many adsorptions of organic substances by activation carbon results foam specific interactions between functional groups on the adsorbate and on the surface of the sorbent. These interactions may be designated as 'specific adsorptions' (Walter, 2012).

Adsorption is the process through which a substance, originally present in one phase, is removed from that phase by accumulation at the interface between that phase and a separate (solid) phase. (Armenante, 2012). Adsorption process has been proved to be an excellent way to treat industrial waste water treatment because the adsorption process has the low-cost, availability, profitability, easy of operation and efficiency （Ayhan Demirbas, 2008).

Adsorption is more approachable and easy to run due to the price of adsorbent that usually is cheap and does not require a pre-treatment step before its application (Wang et al., 2005). A lot of researchers believes this treatment is to be far more superior than others due to variety reasons ((Sanghi and Bhattacharya, 2002; Meshko et al., 2001;Bulut and Aydin, 2006); including the simple design, low cost, and of course easy to handle.

The continuous adsorption in fixed-bed column is often desired from industrial point of view. It is simple to operate and can be scaled-up from laboratory process. The flow behavior and mass transfer aspects become peculiar beyond a particular length to diameter ratio of the column. Adsorption in fixed bed columns using activated carbon has been widely used in industrial effluent, since it does not require the addition of chemical compounds in the separation process (J.M Chern and Y.W Chiem, 2003).

2.2 Types of Adsorption

There are several types of adsorption and each of them has their own different characteristics. Exchange adsorption, physical adsorption and chemical adsorption are examples of types of adsorption.

2.2.1 Exchange Adsorption

Exchange adsorption or ion exchange is the electrostatic due to charged sites on the surface. Adsorption goes up as ionic charge goes up and as hydrated radius goes down. Ion exchange is a highly popular and has been widely practiced in industrial waste water treatment (Sheng et al, 2000).

2.2.2 Physical Adsorption

While in the physical adsorption or physisorption, it focuses on the Van der Waals (weak intermolecular) attraction between adsorbate and adsorbent, which are also responsible for the non-ideal behavior of real gases. The attraction is not fixed to a specific site and the adsorbate is relatively free to move on the surface. This is relatively weak, reversible, adsorption capable of multilayer adsorption. The physical adsorption takes place between all molecules on any surface providing the temperature is low enough. Physical adsorption phenomena were already well known in the early years of the twentieth century, where the various attempts were made to explain the underlying principles (Kenneth, 2008).

2.2.3 Chemical Adsorption

In **c**hemical adsorption or chemisorption, some degree of chemical bonding between adsorbate and adsorbent are characterized by strong attractiveness.

Adsorbed molecules are not free to move on the surface. There is a high degree of specificity and typically a monolayer is formed. The process is seldom reversible. For example of chemical adsorption is the hydrogen takes place on transition metals but not on gold or mercury. Generally some combination of physical and chemical adsorption is responsible for activated carbon adsorption in water and wastewater.

2.3 Activated Carbon

Activated carbon is the most important carbon materials used to adsorb organic solutes from aqueous solution, although the use of activated carbon fibers and activated cloths has been continuously growing in the recent years. These carbon materials are applied in varies system such as drinking water and wastewater treatment and also used in the food, beverage, pharmaceutical and also chemical industries. Furthermore, the activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available environmental control technologies (Carlos, 2008).

Activated carbon is also called activated charcoal or activated coal is carbon produced from the carbonaceous source materials such as nutshells, peat, wood, coal and petroleum pitch. For all three variations of the name, "activated" is sometimes substituted by "active" (Uhrikova, 2007). Activated carbon does not bind well to certain chemicals such as alcohols, strong acids and bases, and most inorganic like sodium, lead and iron. However, the activated carbon can adsorb the iodine very well compare to the others. Activated carbon is produced by a process consisting of pyrolysis of raw material followed by activation with oxidizing gases (Grassi et al, 2012).

The specific surface area of adsorbent affects the adsorption performance. The larger the specific surface area of AC, the better its performance in adsorption process (Gua and Lua, 2003). The optimum specific surface area of activated carbon is between 600 until 1200 m^2/g (Ng et. al, 2002). The adsorption capacity of adsorbent is influenced by its internal surface area and pore volume (Nurul Ain, 2007). Additionally, the effectiveness of activated carbon is depended on their surface chemistry, as well as their pore size distribution (Radovic, 2001). The surface chemistry is influenced by the chemical by its internal surface area and pore volume (Nurul Ain, 2007).

2.4 Types of Activated Carbon

Adsorption is a water treatment process that removes a soluble substance from the water. Adsorption is achieved by an active carbon which comes in two varieties which are Powder Activated Carbon (PAC) and Granular Activated Carbon (GAC), (Grassi et al, 2012). Activation carbon can be manufactured in powder and granular form from a large variety of raw materials and their highly developed porosity, large surface area and variable surface chemistry that make them very unique and versatile adsorbents (Carlos, 2008).

2.4.1 Powder Activated Carbon (PAC)

The powder activated carbon is made from the crushed or ground carbon particles. The particle size typically between 10 and 100μm in diameter .Powder activated carbon is normally used in processing units like, clarifiers, gravity filters and mix basins. Crushed or ground carbon particles are so finely powdered that most of them can easily pass through a designated mesh sieve or sieve. This is because it has small size will form large internal surface having small diffusion distance. The aim of PAC addition is often the removal of unpleasant tastes and odors or, in some cases, toxins produced by blue-green algae (cyanobacteria). In Europe and the Unites States PAC is also used to help control high levels of pesticides or other man made industrial micro pollutants in the source water (Gayle, 2008).

PAC can be added before coagulation, during chemical addition, or during the settling stage, prior to the sand filtration. It is removed from the water during the coagulation process and through filtration. One of the advantages of the PAC is that can be applied for the short period of time and when the problems occurs, then ceased when it is no longer required. With problems that may arise only periodically, for example algal metabolites, or accidental industrial chemical spills, that can be a great cost advantages (Gayle, 2008).

2.4.2 Granular Active Carbon (GAC)

While for the granular activated carbon, it forms smaller external surface because of their larger size as compared to powder activated carbon. The particle size is larger than that of the PAC, usually between o.4 and 2.5 mm.

Granulated carbons are mainly used for treating water. Their main function includes deodorization and separation of components of flow system. It also used to remove the micro pollutants such as pesticides, industrial chemicals and also taste and odors. It also sometimes used to removed natural organic material (NOM), such as humic and fulvic acid, which is present in all water bodies, and reacts with chlorine in the disinfection process to form potentially harmful disinfection by products (Gayle, 2008). The other function of the GAC is used as replacement for sand in conventional treatment filters as this is a low cost alternative to retrofitting GAC filters in an existing plant, where space constrains may not allow additional filters to be built.

Figure 2.1 Types of Activated carbon (Source: Kenneth, 2008):

2.5 Properties of the Activation Carbon

The properties of the activated carbon can be divided into two which are physical properties and chemical properties. Both physical properties and the chemical properties have their own characteristics.

2.5.1 The Physical Properties

The physical properties of the activated carbon are physical attraction of the contaminants to the pore walls of the filtration process. The important physical properties are surface area, product density which is mesh size, abrasion resistance and ash content (Anthony et al, 2012). The amount and distribution of pores are important in determining how well contaminants are filtered. The contaminants are attracted differently depends to the size of the pore filter. Contaminants having large molecules are effectively removed by activated carbon filters. Particle size is an important parameter in specifying carbons for specific applications, which can be affecting such operating of activated carbon, is ash level, which reflects the purity of the carbon. (Robert et al, 2012). Conditions as pressure drop, filtration capabilities, backwash rate requirements and also the rate of adsorption of contaminants. While a smaller particle size will affects more pressure drop across a carbon bed, the rate of diffusion of an organic into the pore and its subsequent adsorption is will be increased.

2.5.2 The Chemical Properties

For the chemical properties of the activated carbon, the filter surface is always interacts chemically with organic molecules. Adsorption may also result by the electrical forces between the activated carbon surface and some contaminants. The activation process also determines the chemical properties of the adsorbing surface. The activation carbon materials that results from various activation processes will posses chemical properties that make them more or less attractive to various contaminants.

2.6 Function of Activated Carbon

Activated carbon or carbon adsorption process is used for removing various organic substances like oils, radioactive compounds, petroleum hydrocarbons, poly aromatic hydrocarbons and various halogenated compounds like chlorine, fluorine, bromine and iodine. (Richardson et al, 2002). Apart from organic compounds it also removes inorganic compounds like arsenic, cadmium, chromium, zinc, lead, mercury, copper and others. As carbon adsorption method is effective in removing pollutants, it is used in following industrial process for water treatment such as ground water purification, the de-chlorination of process water, water purification and also waste water treatment. (Kandasamy et al, 2012).

Activated carbon is an excellent adsorbent because it has a strong affinity for binding organic substances, even at low concentration. Activated carbon also has a vast network of pores of varying size to accept both large and small contaminants molecules and these pores also give activated carbon has a very large surface area. The larger percentage of the total surface area is believed to be of the planar surface type with the attached functional groups (Snoeyink and Weber, 1967). The majority of the adsorption on the surfaces considered because of the relative weak physical or Van der Waals forces (Van der Plas, 1968). On the other hand, the sides of these planar surfaces are attached with many functional groups such as organic carboxyl, phenol and also carbonyl group (Mattson and Mark, 1971) and inorganic oxygen complexes (Snoeyink and Weber, 1967).

The highly porous nature of the carbon provides a large surface area for contaminants to collect. The adsorption takes place because of the attractive force